Coherent Bragg Rod Analysis (COBRA): A New Technique for Structure Determination at Thin-Film Interfaces

Researchers at the Michigan-Howard-Lucent Technologies/Bell Labs Collaborative Access Team (sector 7) have devised a new x-ray method for the direct determination of epitaxial structures: coherent Bragg rod analysis (COBRA). Examples include reconstructed crystal surfaces, interfaces in epitaxial thin films and layered heterostructures, crystalline-amorphous interfaces (Si–SiO_2), and proteins crystallized on a substrate. The high brightness and coherence of the APS undulator radiation enable interference measurements along the characteristic Bragg rods, preserving the *phase* of the scattered x-rays. Using a highly efficient numerical procedure, the complex structure factor (CSF) of the interfacial region is extracted from these interference measurements. Back Fourier transforms of the CSF then provide a complete three-dimensional map of the electron density revealing the structure of the epilayers even far from the interface, as well as distortions in the underlying substrate. Here we describe the application of this novel technique to GaAs passivation layers and note some complementary advantages relative to other methods, such as x-ray holography and x-ray absorption fine structure.

Thin films form the basis of much of current electronics technology. As device dimensions shrink to nanometer levels and nanofabricated composite structures are explored, *interfaces* (between the substrate and passivation layers, magnetic or ferroelectric layers, etc.) play an increasingly critical role. Little is known about the detailed atomic structure at buried interfaces because of the lack of appropriate techniques to probe this region nondestructively.

In this work, carried out at the Michigan-Howard-Lucent Technologies/Bell Labs Collaborative Access Team (MHATT-CAT) and Pacific Northwest Consortium (PNC) CAT undulator beamlines, we have devised [1] a powerful solution to the problem of determining the structure of thin-film interfaces, utilizing the high-brightness characteristics of the Advanced Photon Source (APS) undulator radiation. The method we have developed is quite general and can be applied to any structure, crystalline or otherwise, that is deposited on an epitaxial (i.e., crystallographically oriented) substrate.

We describe our approach with reference to a specific example in electronic materials research: a thin (~5 nm) epitaxial layer of Gd_2O_3 deposited by molecular beam epitaxy (MBE) on a (100) GaAs wafer, of interest for its potential as an effective passivation layer for GaAs devices [2]. The x-ray scattering from such a system is composed of sharp Bragg peaks from the GaAs substrate, together with continuous ridges of scattered intensity (Bragg rods) associated with the truncation of the GaAs crystal.

The intensity profile along the Bragg rods contains information about the 3D arrangement of atoms in the vicinity of the GaAs–Gd_2O_3 interface. In conventional, incoherent x-ray scattering, in which the phase of the x-rays scattered at each position along the Bragg rod is indeterminate, it becomes an intractable problem to determine precise atomic positions. However, by using an x-ray beam that is *coherently* diffracted—straightforward to do at a high-brilliance source such as APS—we can keep track of the relative phase at each position along the Bragg rod.

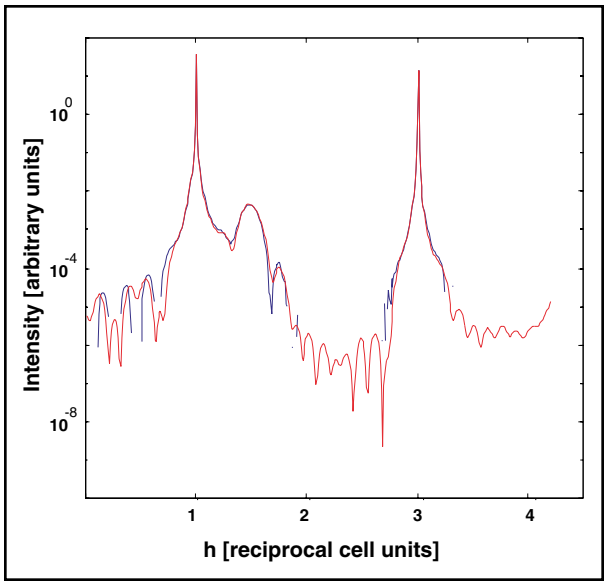

FIG. 1. (h,-1,1) Bragg rod intensity profiles of the 5 nm epitaxial Gd_2O_3 film on (100) GaAs. The blue trace is the data and the red curve is the absolute value squared of the CSF calculated from the 3D electron density that we obtained.

The approach is somewhat analogous to laser holography, in which the reflected (diffracted) beam is brought into interference with a coherent reference beam, the intensity of which is adjusted to approximately match that of the reflected beam. The reference beam in this experiment is essentially derived from the periodic components of the sample and is dominated by the substrate. Using the fact that the undulator beam has a high degree of transverse coherence, we can determine the amplitude and phase at each point along the Bragg rod and thereby extract the real and imaginary components of the scattering factor. Once the complex scattering factor (CSF) is determined, it is a straightforward matter to invert this data (using back-Fourier transform) to arrive at the three-dimensional (3D) electron density map corresponding to the unknown structure. Further details can be found in Yacoby et al. [1].

We have successfully tested the method described above on a known model system consisting of a few layers of AlAs buried just below the surface of a (110)-oriented GaAs wafer [3,4]. Having established the validity of the method using a known system, we proceeded to apply the technique to investigate the structure of the Gd_2O_3–GaAs interface. Previous work by Bolliger et al. [5] has shown that the Gd_2O_3 film grows in such a way that 3 Gd_2O_3 unit cell edges are approximately commensurate with 4 GaAs diagonals with one Gd_2O_3 diagonal matching two GaAs diagonals, and that the film tends to grow as a single domain.

We have measured the diffraction intensity along the Bragg rods within a volume defined by $h,k,l \leq 4$. Figure 1 shows a portion of the Bragg rod data for this system. By comparing the intensity profiles in symmetry-equivalent directions, we were able to confirm that the system is indeed a single domain. Altogether, we were able to probe 13 symmetry-inequivalent Bragg rods at an x-ray energy of 10 keV.

The amplitude and phase of the scattering factor of the unknown electron density were calculated and then back-Fourier transformed into real space to obtain the 3D electron density. In Fig. 2 we show the electron density calculated from the total complex scattering factor, as a function of distance from the interface. We point out several interesting findings:

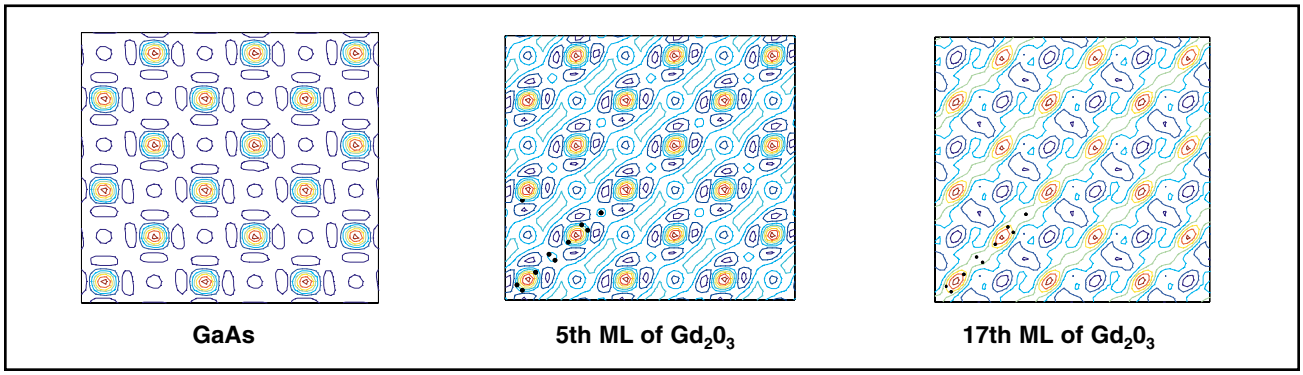

FIG. 2. Electron density maps of layers at different distances from the interface between an epitaxial Gd_2O_3 film and its interface with a (100) GaAs substrate, as derived from the coherent Bragg rod method. The black dots depict the ideal positions of the Gd atoms, projected onto the 2D GaAs unit cell.

close to the interface, we see a strong tendency of the Gd atoms to shift away from their bulk sites (denoted by the green dots) and to occupy positions that more closely conform to the GaAs structure. The Gd atoms thus form "stripes" along the GaAs diagonals shown in Fig. 2. By fitting the electron density in real space, we are able to determine the positions of the Gd atoms with sub-Å resolution and see a systematic shift from layer to layer going away from the interface. It is interesting to note that the influence of the GaAs persists to at least 17 Gd_2O_3 monolayers. This tendency to conform to the underlying substrate provides insight about why Gd_2O_3 is an effective passivation layer for GaAs.

Our work demonstrates that it is possible to obtain 3D electron density maps of an epitaxial interface with sub-angstrom resolution. Our method has complementary advantages over existing techniques such as x-ray holography [6] and XAFS, both local probes which average over inequivalent atomic positions. Because Bragg rod scattering is sensitive to 2D periodic structure, our approach is capable of distinguishing these subtle features. Moreover, unlike cross-sectional TEM, which provides structural information over a local region and requires sample preparation that may disrupt subtle features, our new technique is non-invasive and provides information on positional correlations that can be compared with theoretical models. The method is quite general and the fact that computation time scales linearly with the number of atoms, rather than geometrically as in a conventional intensity refinement procedure, means that it can be used on systems with very large 2D unit cells. For example we analyzed the simulated data of an organic molecule with about 1000 atoms arranged in a 2D array on a molecular crystal and reconstructed faithfully its structure. This work further shows that the electron density obtained in this way has a wealth of structural information including subtle features such as the long range influence of the GaAs substrate on the Gd positions within the unit cell. This sensitivity to fine atomic details will make the method especially useful for studies of ferroelectric thin films, an area we are currently exploring.

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